

MEASUREMENT OF RADIONUCLIDES USING ION CHROMATOGRAPHY AND FLOW-
CELL SCINTILLATION COUNTING WITH PULSE SHAPE DISCRIMINATION

Robert. A. Fjeld (fjeld@clemson.edu; 864-656-5569)

Timothy. A. DeVol (devol@clemson.edu; 864-656-1014)

Alena Paulenova (apaulen@clemson.edu; 864-656-1009)

J. Roane (jroane@clemson.edu)

H. Tan (htan@clemson.edu)

J. Zimmerly (jzimmer@clemson.edu)

Department of Environmental Engineering and Science

Clemson University

L.G. Rich Environmental Research Laboratory

Clemson Research Park

342 Computer Court

Anderson, SC 29625-6510

and

John. D. Leyba (john.leyba@srs.gov; 803-725-4180)

Westinghouse Savannah River Co.

Bldg. 773-41A, Room 135

Aiken, SC 29808

Research sponsored by the U.S. Department of Energy
Federal Energy Technology Center, Morgantown, West Virginia
under
Contract DE-AR21-95MC32110

ABSTRACT

Radiological characterization and monitoring is an important component of environmental management activities throughout the Department of Energy complex. Radionuclides which cannot easily be detected by gamma-ray spectroscopy, such as pure beta emitters and transuranics, pose special problems because their quantification generally requires labor intensive radiochemical separations procedures that are time consuming and impractical for field applications. This project is focused on a technology that can measure transuranics and pure beta emitters relatively quickly and has the potential of being field deployable. The technology combines ion exchange liquid chromatography and on-line alpha/beta pulse shape discriminating scintillation counting to produce simultaneous alpha and beta chromatograms. The project consisted of the following tasks: (1) development of a low background, flow-cell detector, (2) identification of potential sample chemical and radiological interferences, (3) development of protocols for processing waste and/or environmental samples, and (4) integration and testing of the prototype system. Presented here are the results for Task 4 including (i) characterization of the granular Parylene C coated CsI:Tl scintillator, which is the key component of the pulse shape discriminating flow-cell detection system; (ii) completion of a digital pulse shape discrimination system which not only significantly reduces the hardware requirements but also is more user friendly than the analog system; (iii) integration of the sample processing, chromatography, and detection components of the system into a single integrated unit; and (iv) testing of the integrated system for a group of surrogate and real samples that are representative of the spectrum of matrices encountered at DOE sites.

INTRODUCTION

Radiological characterization and monitoring needs in support of environmental restoration and waste management activities at Department of Energy (DOE) facilities are extensive and diverse. Radionuclides which cannot easily be detected by gamma-ray (^{90}Sr , ^{99}Tc , and ^{63}Ni) and actinides (e.g. ^{232}Th , $^{235,238}\text{U}$, ^{237}Np , $^{238,239,240,241}\text{Pu}$, ^{241}Am) pose special problems because their quantification generally requires labor intensive radiochemical separations procedures that are time consuming and generally not practical for field-based measurements. The technology described here addresses a generic need for “field-deployable instrumentation for the determination of isotopes and isobars” (DOE, 1993). Our approach combines liquid chromatography and flow cell scintillation counting with alpha/beta pulse shape discrimination.

The basic instrumentation upon which our system is based was purchased in the early 1990's. In its original commercial form, the instrumentation was capable of separating select activation/fission products in ionic forms from relatively pure aqueous samples. We subsequently developed the capability of separating and detecting actinides (thorium, uranium, neptunium, plutonium, americium, and curium) in less than 30 minutes (Reboul and Fjeld, 1993) and realized that the potential time savings over traditional radiochemical methods for isolating some of these radionuclides was enormous. However, at that time, the technique had only been used for radionuclide concentrations that were considerably above environmental levels and for aqueous samples of relatively high chemical purity. For the technique to be useful in environmental applications, development work was needed in lowering detection limits; to be useful in applications involving non-aqueous matrices such as soils and sludges or complex aqueous matrices such as those encountered in waste samples, development work was needed in sample preparation and processing.

OBJECTIVE

The general goal of our development effort was to address these issues, and transform an interesting laboratory technique of limited applicability into a robust, field

deployable system for relatively rapid analysis of non-gamma emitting activation/fission products and transuranics in various wastes and environmental media.

The development effort consisted of four tasks. In the first three tasks, the technical feasibility of the technology was demonstrated (Fjeld, et al. 1998). The principal purpose of the final task, and the subject of this paper, was to fabricate and test a laboratory prototype system. The subtasks were: (i) performance testing of the scintillator used in the flow-cell detector; (ii) further development of a digital pulse shape discrimination system; (iii) integration of the sample processing, chromatographic separation, and radiation detection components into a prototype bench-scale system; and (iv) the analysis of sample surrogates (groundwater from the southeastern U.S. and basalt from the Idaho National Engineering and Environmental Laboratory) spiked with targeted radionuclides and actual samples (supernatant from a high activity drain tank at the Savannah River Technology Center and sludge from a high level waste tank at the Savannah River Site).

APPROACH / PROJECT DESCRIPTION

The system is illustrated schematically in Figure 1. Samples are processed to yield an aqueous solution with the radionuclides in an ionic form. The ions are concentrated on an ion exchange column and subsequently removed to a separation column with chemical eluents. Through the selection and sequencing of the eluents, chromatographic separation of the constituents is achieved. A chromatogram of radioactive constituents is then produced by an on-line scintillation counter which yields separate but simultaneous chromatograms for alpha emitters and beta emitters through pulse shape discrimination. The flow-cell detector contains CsI:Tl particles coated with Parylene C. For low-level applications, fractions containing selected radionuclides can be collected and counted off-line. Radionuclides are identified through characteristic elution times, and their concentrations are determined from the integrated counts under the peak of interest, the detection efficiency, the yield of the sample processing procedure, and the volume or mass of the original sample.

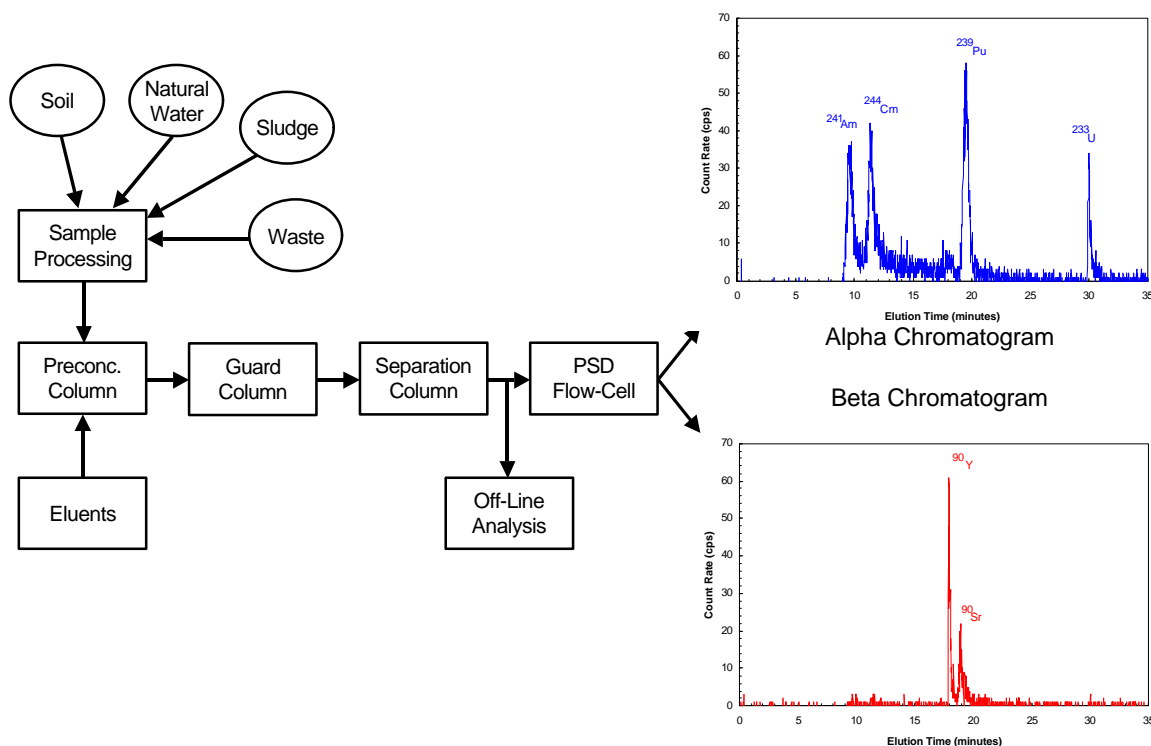


Figure 1. Simultaneous measurement of alpha and beta emitters by ion chromatography and the pulse shape discrimination flow-cell system of a groundwater sample spiked with radioactivity.

Three transportable equipment cabinets were used to house the sample processing, ion chromatography, and data acquisition components of the laboratory prototype (Figure 2). The sampling processing cabinet (left cabinet in Figure 2) houses the microwave oven, hot plates, and extraction chromatographic columns. The ion chromatography cabinet (middle cabinet in Figure 2) houses the chemical eluents, gradient pump, and ion chromatography unit. The electronics cabinet (right cabinet in Figure 2) houses the analog pulse shape discrimination.



Figure 2. Photograph of the laboratory prototype. The left cabinet is for sample processing, the middle cabinet houses the ion chromatography system and the right cabinet contains the analog pulse shape discrimination system. The flow-cell is housed in the black box that is atop the middle and right cabinets.

RESULTS

Parylene C Coated CsI:Tl

The coating thickness of the Parylene C coated CsI:Tl particles is expressed as the ratio of coating mass to particle mass. Coating thicknesses of 3%, 4%, and 5% were evaluated to determine cell half life and radiation detection efficiencies. This was accomplished by monitoring the count rate from the flow-cell as a function of time following a semi-infinite step input of a radionuclide standard. The integrity of the coating was quantified through the half life, which is the time required for the efficiency to decrease by a factor of two. The alpha-particle detection efficiency, ϵ_{α} , was the

average of the first 10 minutes of three flow-cell lifetime tests. The beta-particle detection efficiency, ϵ_β , was determined from the chromatograms of radionuclide standards. Tests were conducted for two particle sizes, 63 – 90 μm and 90 – 125 μm particles. The results for these tests are given in Table 1.

TABLE 1. Summary of detection efficiency and half life of the Parylene C Coated CsI:TI data for the 63-90 μm and 90-125 μm granules.

	CsI(Tl) coated with 3% Parylene C			CsI(Tl) coated with 4% Parylene C			CsI(Tl) coated with 5% Parylene C		
	ϵ_α	ϵ_β	$\tau(\text{hr})$	ϵ_α	ϵ_β	$\tau(\text{hr})$	ϵ_α	ϵ_β	$\tau(\text{hr})$
63-90 μm	67%	34%	5.2 (77%)	41%	24%	3.4 (93%)	32%	11%	4.0 (94%)
90-125 μm	59%	31%	5.1 (87%)	42%	21%	2.0 (95%)	30%	11%	4.1 (92%)

α is ^{241}Am , β is ^{90}Y , and τ is the flow-cell lifetime as determined for an alpha emitter (fraction of the total cell half time with the specified half life)

Digital PSD System

The digital pulse shape discrimination system condenses the data acquisition system to a computer card and computer. A data acquisition program was written using National Instruments, Inc. LabVIEW V 5.1. The program involves three integrated steps. First, if the leading edges of the individual PMT pulses are within 100 ns of one another, the pulses are considered to be in coincidence. Second, if the pulses are coincident, they are aligned in time and summed. Third, the summed pulse is processed to produce pulse shape and pulse height spectra. On-line and off-line analyses of the data were used to optimize the alpha and beta regions-of-interest in the single parameter pulse shape and dual parameter spectra. The software has a real-time indicator which displays the total (alpha + beta) count rate, thus providing a real-time chromatogram for qualitative analysis. The dual-parameter spectrum and alpha/beta chromatogram are subsequently generated by post-processing the data stored in computer memory after the chromatograph run finishes (Figure 3). The digital data acquisition system thus provides the following features: (1) real-time count rate; (2) pulse height and pulse shape spectra; (3) 2D and 3D dual-parameter spectra; (4) alpha and beta chromatograms.

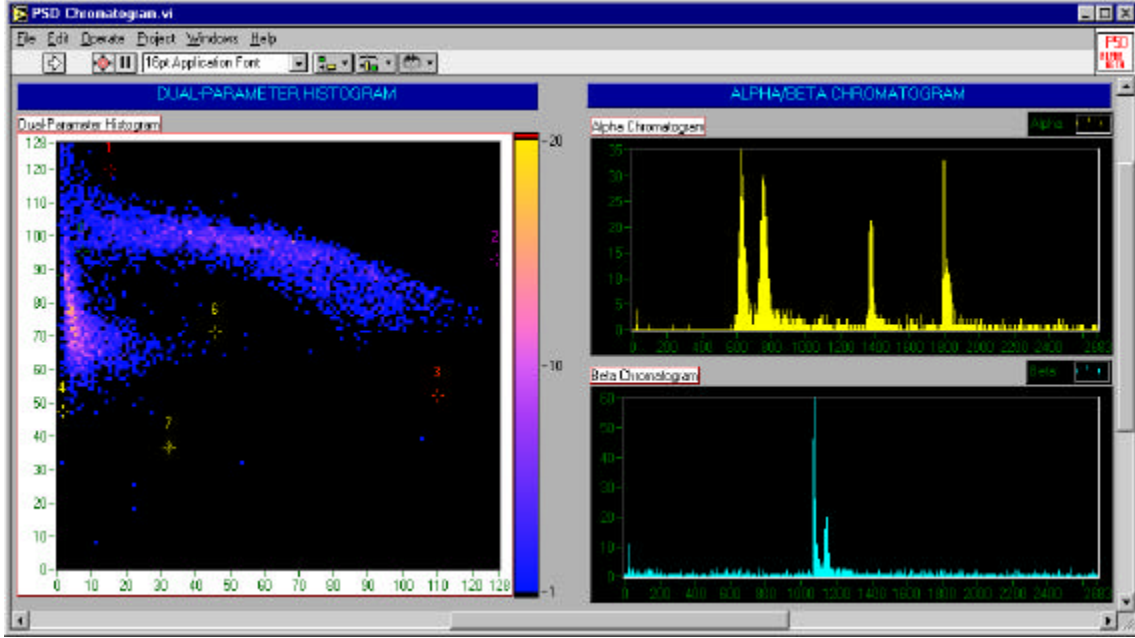


Figure 3. Data display for the digital dual parameter pulse shape discriminating data acquisition system.

The digital system was benchmarked against an analog data acquisition system. Digital and analog pulse height chromatograms for CsI:Tl, CaF₂:Eu, and scintillating glass (GS-20) flow cells were compared. There was good correlation between the digital system and the analog system.

A disadvantage of the digital system is the dead time, which is due primarily to the transfer of digitized data from the oscilloscope memory to the computer memory and software processing and display of the digitized data. To decrease the dead time the digital system was modified by upgrading from LabVIEW 4.1 to 5.1 and upgrading the computer from P5 – 200 MHz to PIII – 450 MHz. These modifications reduced the dead time by a factor of 2 – 3. Modification of the LabVIEW code interface node (CIN) expedited data acquisition and dead time was reduced by an additional factor of two to approximately 2 ms. Additional reductions could be achieved by hardware implementation of the data processing. A summary of the operational characteristics of the digital system used in conjunction with the CsI:Tl detector is given in Table 2.

TABLE 2. Characterization of the digital data acquisition system with CsI:Tl and aqueous solutions of $^{90}\text{Sr}/^{90}\text{Y}$ and ^{233}U

Property		Single Parameter	Dual Parameter
FOM	$^{90}\text{Sr}/^{90}\text{Y}$ ^{233}U	1.65	—
Detection Efficiency (%)	$^{90}\text{Sr}/^{90}\text{Y}$	26.4	26.0
	^{233}U	31.3	30.4
Background Count Rate (cps)	α	0.31	0.05
	β	0.84	0.69
Spillover (%)	α to β	2.1	1.3
	β to α	1.4	0.3

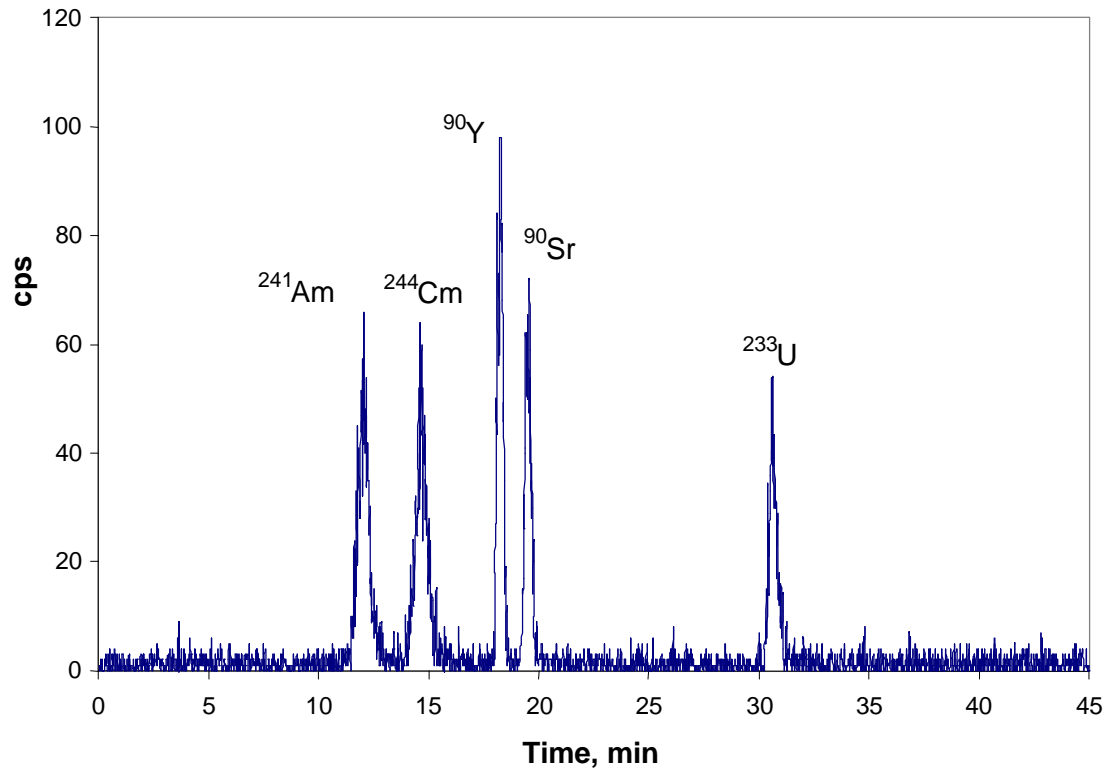


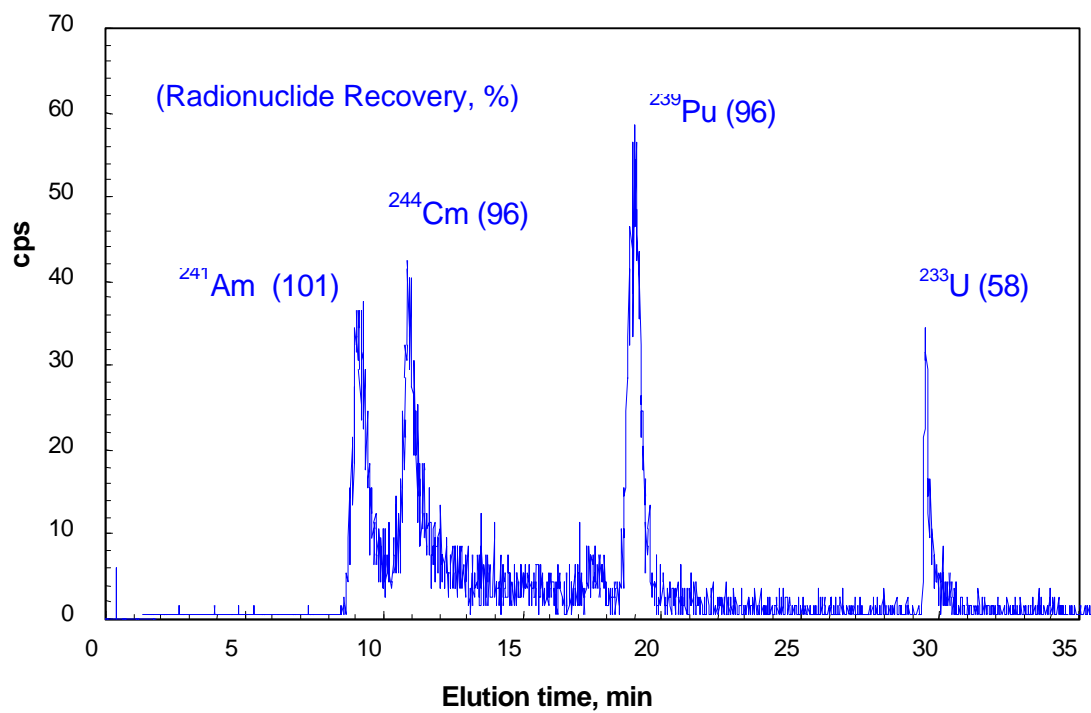
Figure 4. Chromatogram of Strontium / Actinide Standard obtained with a glass scintillator flow-cell (non-pulse shape discriminating)

Sample Analyses

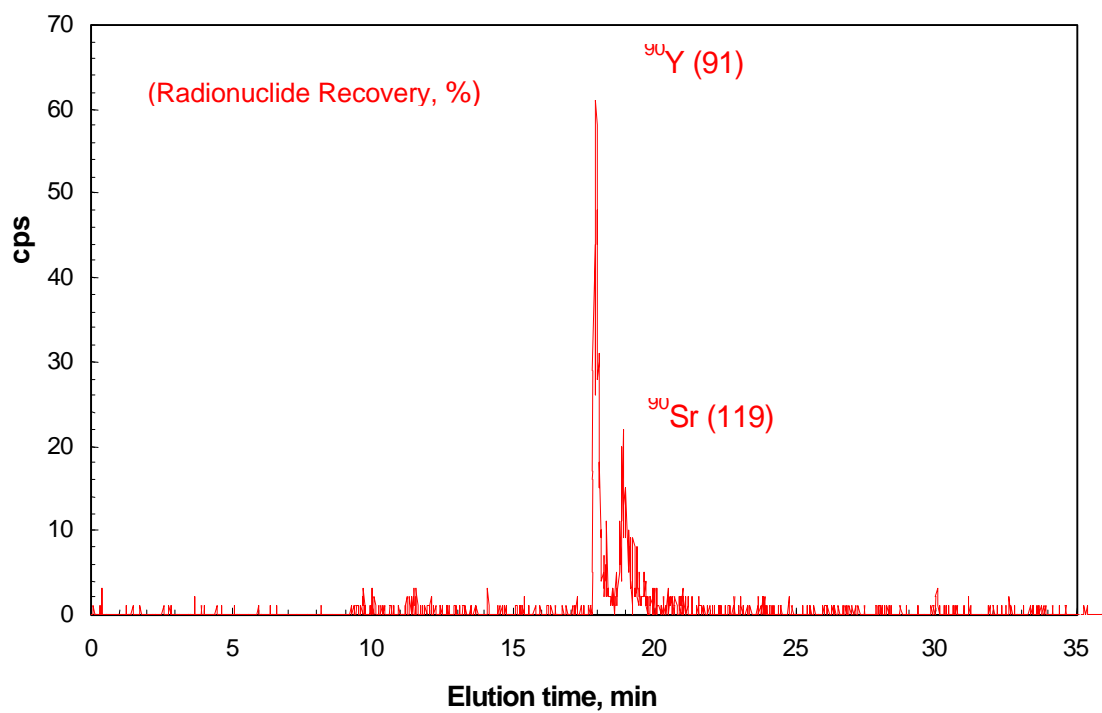
The laboratory prototype was tested for two surrogate samples and two actual samples that are representative of the spectrum of matrices encountered at DOE sites. The surrogates, a groundwater from the southeastern U.S. and basalt from INEEL, were spiked with a strontium/actinide standard developed previously (Figure 4). The actual samples were supernatant from the high activity drain tank at SRTC and sludge from a waste tank at SRS.

Groundwater from the southeastern U.S. was spiked with both the strontium/actinide standard and with plutonium. Plutonium was added because its elution time in the chromatography column is the same as strontium, and we wanted to test the ability of the PSD detector to discriminate between the two. The alpha and beta chromatograms for the sample are presented in Figure 5, (a) and (b), respectively. The data were obtained using a 4% 90-125 μm Parylene C coated CsI:Tl flow-cell. The resolution of these chromatograms was essentially the same as the standard (Figure 4), and the recoveries exceeded 90% for all of the radionuclides except for uranium (58%).

Basalt from INEEL was also spiked with the strontium/actinide standard. However, analyses of digested samples were unsuccessful, and the decision was made to leach the samples with nitric acid rather than to digest them. In this test, 0.5 g of basalt was spiked with 1 mL of the strontium/actinide standard (~240 Bq of each radionuclide), leached with nitric acid, and processed. The resulting solution was diluted by a factor of five. The combined alpha/beta chromatogram (obtained using a glass flow cell) is presented in Figure 6. The resolution was excellent, but the recoveries were very poor, especially for uranium. We believe the low recoveries occurred because actinides form complexes with phosphate from the basalt. These complexes affect the yield of the chromatographic extraction. The identification of the phosphate interference is consistent with our previous finding that the processing protocol may need to be modified for some complex matrices.



(a)



(b)

Figure 5. Alpha (a) and beta (b) chromatograms from a spiked groundwater sample.

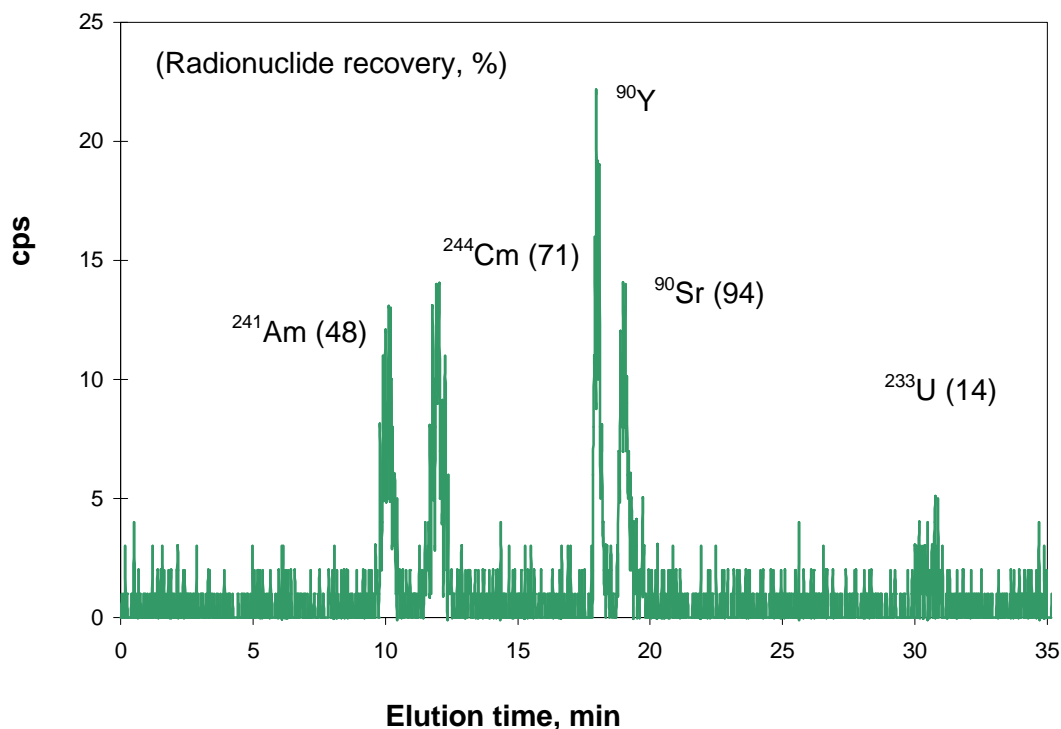
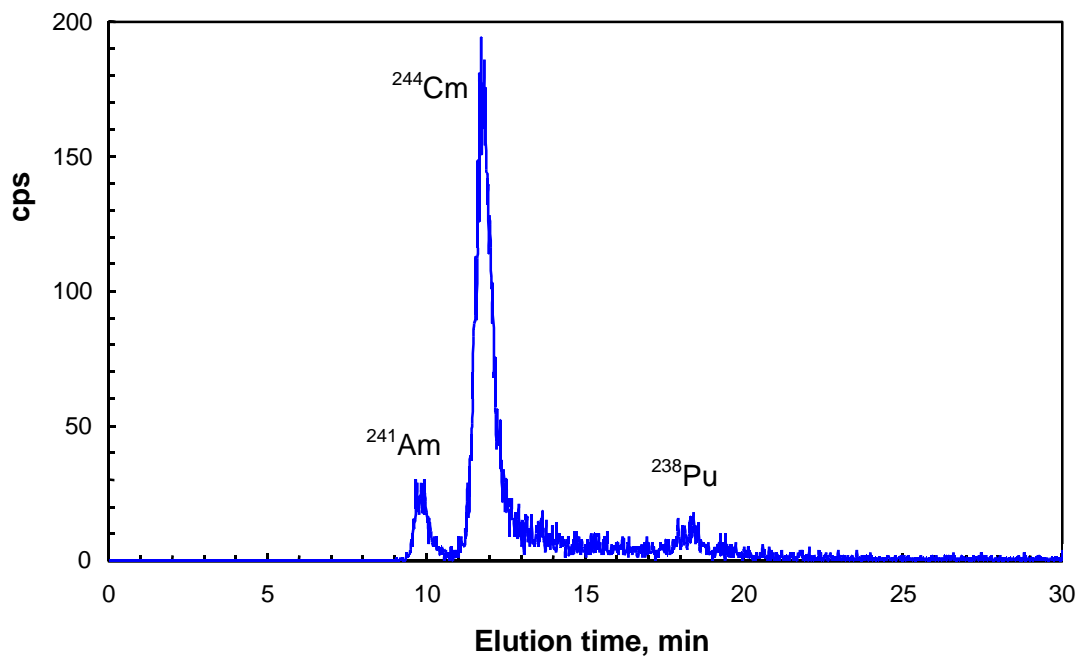
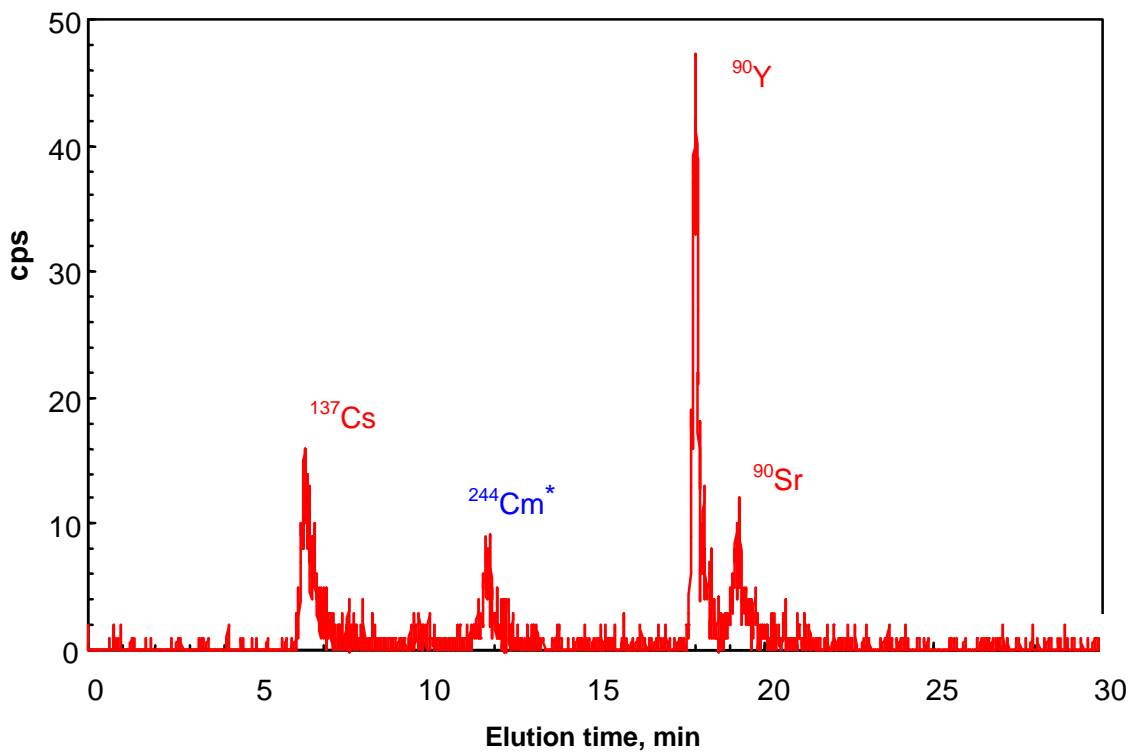


Figure 6. Chromatogram for basalt leached with nitric acid.

The SRTC high-activity drain tank receives liquid laboratory wastes. A 0.25 mL sample was analyzed without processing. The chromatograms are presented in Figure 7. Based on elution times, plutonium, americium, and curium were detected in the alpha chromatogram; and cesium, strontium, and yttrium were detected in the beta chromatogram. There was some spillover of curium in the beta chromatogram. Presented in Table 3 is a comparison of concentrations as measured in our system and as measured at SRTC. Our analyses were all within 20% of those from SRTC.



(a)



(b)

Figure 7. Alpha (a) and beta (b) chromatograms for the supernatant form the high activity drain tank at SRTC.

TABLE 3. Summary of High Activity Drain Tank Sample. Data obtained using a 4% 90-125 μm Parylene C coated CsI:Tl flow-cell.

Radionuclide	SRTC Measurement (Bq mL ⁻¹)	Our Measurement (Bq mL ⁻¹)
⁹⁰ Sr	-	1130
¹³⁷ Cs	1557	1880
²³⁸ Pu	828	690
²⁴¹ Am	1165	1080
²⁴⁴ Cm	10656	10020

A sample of sludge was obtained from the archives for SRS High Level Waste Tank 8. At SRTC, 0.125 grams of the sample was dissolved into 100 mL of 0.1 M HNO₃ of which 10 mL was shipped to our laboratory. A 0.25 mL aliquot was analyzed without processing. The chromatograms are presented in Figure 8. Cesium, strontium and yttrium were detected in the beta chromatogram; and plutonium, americium and curium were detected in the alpha chromatogram. A comparison of the analyses is presented in Table 4. Our analyses were within 15% of the SRTC analyses for strontium, americium and curium and within 30% for cesium. Our plutonium analysis was less than the SRTC analysis by almost a factor of two.

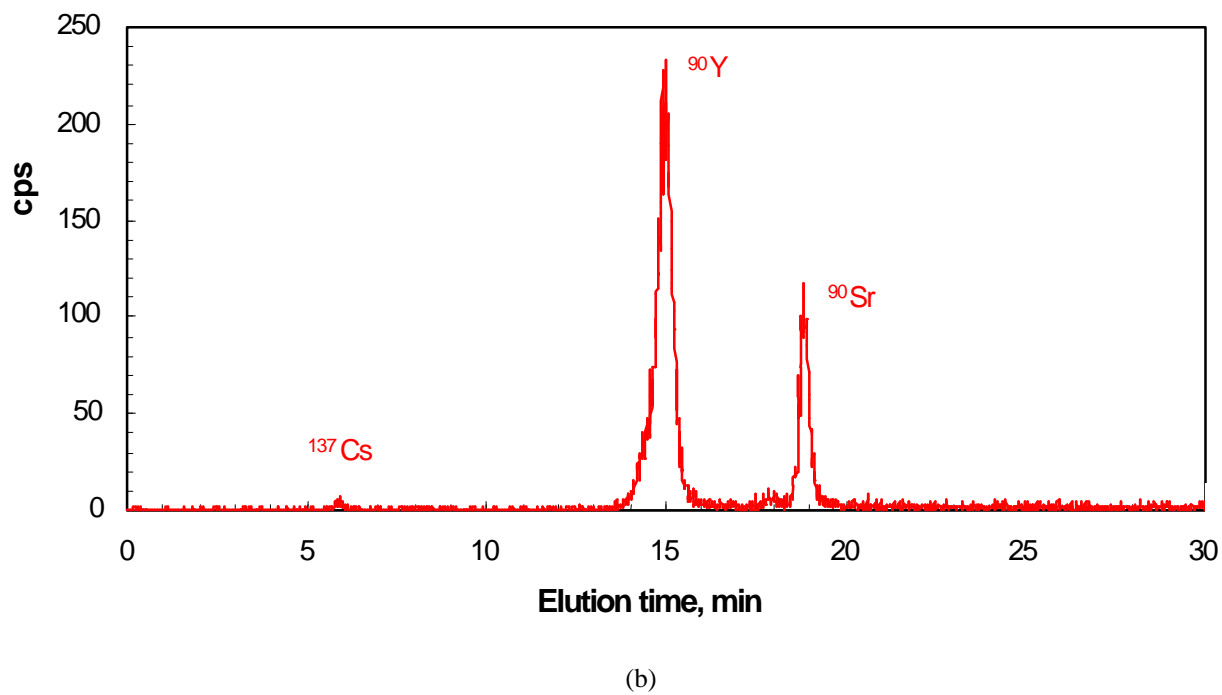
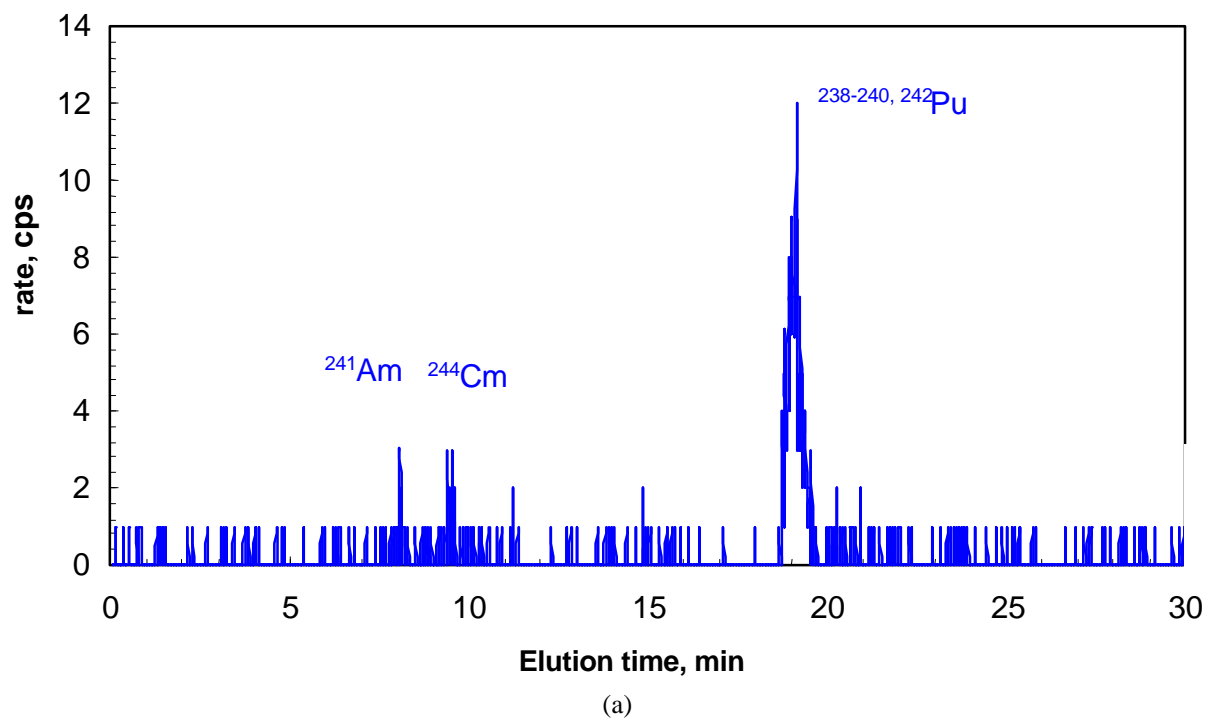


Figure 8. Alpha (a) and beta (b) chromatograms from a SRS HLW sludge.

TABLE 4. Summary of the HLW sludge sample analysis. Data obtained using a 3% 63 - 90 μm Parylene C coated CsI:Tl flow-cell.

Radionuclide	SRTC Measurement (Bq mL ⁻¹)	Our Measurement (Bq mL ⁻¹)
⁹⁰ Sr	33,300	28,410
¹³⁷ Cs	1170	850
^{238-240,242} Pu	920	640
²⁴¹ Am	45	41
²⁴⁴ Cm	60	54

APPLICATIONS / BENEFITS

The laboratory prototype is capable, with some limitations, of analyzing alpha and beta emitters in samples that are representative of many of those encountered in the DOE complex. The limitation is that modifications of the sample processing protocol may be required for some complex matrices, specifically soils. Nonetheless, based on the success of the laboratory prototype, a field demonstration is warranted.

The principal advantages of the technology are (1) its ability to analyze a mixture of alpha and beta emitters in a relatively short period of time, much less than that required by traditional techniques and (2) its relatively small size makes it amenable to field deployment. This translates into both a cost advantage and an operational advantage, especially in field applications. Estimates of the capabilities, in terms of analysis time and minimum detectable concentration, are presented in Table 5.

TABLE 5. Summary of expected detection limits and analysis times for aqueous and solid samples.

	Aqueous Sample		Solid Sample
	4 hour analysis (on-line counting)	24 hour analysis (off-line counting)	48 hour analysis (off-line counting)
Strontium-90	4000 pCi L ⁻¹ (160 kBq/m ³)	12 pCi L ⁻¹ (0.4 kBq/m ³)	5 pCi g ⁻¹ (0.2 kBq/Kg)
Transuranics	1500 pCi L ⁻¹ (60 kBq/m ³)	3 pCi L ⁻¹ (0.1 kBq/m ³)	1 pCi g ⁻¹ (0.04 kBq/Kg)

REFERENCES

- R. A. Fjeld, T. A. DeVol, and J. D. Leyba, "Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting with Pulse Shape Discrimination: Final Report for Base Phase," Clemson University, 1998.
- T.A. DeVol, H. Tan and R.A. Fjeld, "Dual Parameter Analysis of CsI:Tl/PMT with a Digital Oscilloscope," accepted for publication in *Nucl. Instr. and Meth.*
- T. A. DeVol, S. B. Chotoo, R. A. Fjeld, " Evaluation of granulated BGO, GSO:Ce, YAG:Ce, CaF₂:Eu and ZnS:Ag for alpha/beta pulse shape discrimination in a flow-cell radiation detector," *Nucl. Instr. and Meth.*, A425 (1999) 228-231.
- J. E. Roane, T.A. DeVol, J.D. Leyba and R.A. Fjeld, "Effects of Ionic Radiological and Chemical Interferences on the Chromatographic Separation of a Radionuclide Standard Solution," *J. Radioanalytic and Nuclear Chemistry* Vol. 240, No. 1 (1999) 197-208.
- K. H. Hastie, T.A. DeVol and R.A. Fjeld, "Development of a Homogeneous Pulse Shape Discriminating Flow-Cell Radiation Detection System," *Nucl. Instr. and Meth.*, A422 (1999) 133-138.
- S. D. Chotoo, T. A. DeVol and R. A. Fjeld, "Development of a Heterogeneous Pulse Shape Discriminating Flow-Cell using Polymer Coated CsI:Tl," *IEEE Trans. Nucl. Sci.*, Vol. 44, No. 4 (1997) 1630-1634.

ACKNOWLEDGEMENTS

We express our appreciation to Ms. Sandra Clipp for providing administrative support. We also appreciate the support provided by Jagdish Malhotra, the FETC Contracting Office's Representative.